

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE FORM PTO-1390 (REV 11-98)		ATTORNEY'S DOCKET NUMBER Mo-5845/LeA 32,871
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>		U S APPLICATION NO (If known see 37 CFR 1.5) To Be Assigned <b>09/601152</b>
INTERNATIONAL APPLICATION NO. PCT/EP99/00035	INTERNATIONAL FILING DATE January 7, 1999	PRIORITY DATE CLAIMED February 6, 1998
TITLE OF INVENTION Method for Regenerating Supported Catalysts Covered with Gold Particles ...		
APPLICANT(S) FOR DO/EO/US WEISBECK, Markus, et al.		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND or SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))           <ul style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ul> </p> <p>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))           <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ul> </p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>		
Items 11. to 16. below concern document(s) or information included:		
<p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p><input type="checkbox"/> A <b>SECOND or SUBSEQUENT</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information: Abstract Form PTO 1449 w/references</p>		

U.S. APPLICATION NO. (if known) see 37 CFR 1.492(a)(1)

To Be Assigned **09/601152**INTERNATIONAL APPLICATION NO  
PCT/EP99/00035ATTORNEY'S DOCKET NUMBER  
Mo-5845/LeA 32,871

17.  The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5))**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$970.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$840.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$760.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$670.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$96.00

**CALCULATIONS PTO USE ONLY****ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$ 840.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than  20  30 months from the earliest claimed priority date (37 CFR 1.492(c)).

\$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	6 -20 =	0	X \$18.00	\$ 0.00
Independent claims	1 -3 =	0	X \$78.00	\$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+\$260.00	\$ 0.00
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ 840.00
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$ 0.00
<b>SUBTOTAL =</b>				\$ 840.00
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ 0.00
<b>TOTAL NATIONAL FEE =</b>				\$ 840.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property				\$ 0.00
<b>TOTAL FEES ENCLOSED =</b>				\$ 840.00
				<b>Amount to be: refunded</b> \$
				<b>charged</b> \$

a.  A check in the amount of \$\_\_\_\_\_ to cover the above fees is enclosed.

- b.  Please charge my Deposit Account No. 13-3848 in the amount of \$840.00 to cover the above fees. A duplicate copy of this sheet is enclosed.
- c.  The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO

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00157  
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29,457

REGISTRATION NUMBER

09/601152  
534 Rec'd PCT/PT 27 JUL 2000

PATENT APPLICATION  
Mo5845  
LeA 32,871

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF )  
MARKUS WEISBACK ET AL ) PCT/EP99/00035  
)  
SERIAL NUMBER: TO BE ASSIGNED )  
)  
FILED: HEREWITH )  
)  
TITLE: METHOD FOR REGENERATING )  
SUPPORTED CATALYSTS COVERED )  
WITH GOLD PARTICLES AND USED )  
FOR OXIDIZING UNSATURATED )  
HYDROCARBONS )

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Upon granting a Serial Number and filing date to the enclosed application,  
please amend this application as follows:

IN THE SPECIFICATION:

At page 1, lines 1-2, please delete the title in its entirety and substitute  
therefor - - Method for Regenerating Supported Catalysts Covered with Gold  
Particles and Used for Oxidizing Unsaturated Hydrocarbons- -.

"Express Mail" mailing label number EK983331152US  
Date of Deposit July 27, 2000

I hereby certify that this paper or fee is being deposited with the United States  
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of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)



Signature of person mailing paper or fee

After page 12, please add the following:

**--ABSTRACT OF THE DISCLOSURE**

The activity of catalysts composed of gold particles on a titanium dioxide or hydrous titanium dioxide support is regenerated by contacting those catalysts with water, dilute acid or dilute hydrogen peroxide solution. These regenerated catalysts may be used for the oxidation of unsaturated hydrocarbons.--

**IN THE CLAIMS:**

Please cancel Claims 1-5.

Please add the following new Claims 6-11:

6. A method for regenerating catalytic activity of a catalyst composed of a titanium dioxide or hydrous titanium dioxide support coated with gold particles that has been used for the oxidation of unsaturated hydrocarbons in the gas phase comprising contacting the catalyst with water, dilute acid or a dilute hydrogen peroxide solution.

7. The method of Claim 6 in which the catalyst being regenerated was produced by a deposition-precipitation method.

8. The method of Claim 6 in which the catalyst being regenerated is contacted with steam under pressure.

9. The method of Claim 6 in which the catalyst being regenerated is contacted with an aqueous hydrogen peroxide solution having a concentration less than or equal to 10%.

10. The regenerated catalyst produced by the method of Claim 6.

11. A process for the oxidation of unsaturated hydrocarbons with molecular oxygen in the presence of hydrogen in the gas phase in the presence of the regenerated catalyst of Claim 10.--

**REMARKS**

The specification has been amended at page 1 to change the title to that which appears on the corresponding published application WO 99/39827.

An Abstract of the Disclosure has been added. A copy of the Abstract page is enclosed.

Claims 1-5 have been cancelled and rewritten in a form more commonly used in U.S. practice.

New Claim 6 corresponds substantially to original Claim 1.

New Claim 7 corresponds substantially to original Claim 2.

New Claim 8 corresponds substantially to original Claim 3.

New Claim 9 corresponds substantially to original Claim 4.

New Claim 10 is directed to the regenerated catalyst produced by the method of Claim 6. Support for this claim is found in Examples 1-10 of the specification.

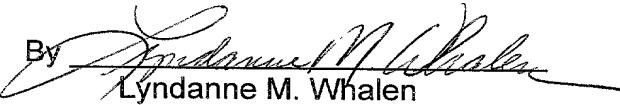
New Claim 11 is directed to a process for the oxidation of unsaturated hydrocarbons in which the catalyst used is one which has been regenerated by the method of Claim 6. Support for this claim is found in original Claim 5.

The above amendments are believed to place this application in better form.

An action on the merits is respectfully requested.

Respectfully submitted,

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534 Rec'd PCT/PTC 27 JUL 2000

A method of regenerating support catalysts coated with gold particles for the oxidation of unsaturated hydrocarbons

This invention relates to a method of regenerating catalysts for the catalytic 5 production of epoxides from unsaturated hydrocarbons by oxidation with molecular oxygen in the presence of molecular hydrogen in the gas phase, and also relates to the use of these regenerated catalysts for the oxidation of unsaturated hydrocarbons.

The direct oxidation of unsaturated hydrocarbons with molecular oxygen in the gas 10 phase does not normally proceed below 200°C - even in the presence of catalysts, and it is therefore difficult selectively to produce oxidation products which are susceptible to oxidation, such as epoxides, alcohols or aldehydes for example, since subsequent reactions of these products frequently proceed more rapidly than the oxidation of the olefines themselves which are used.

15 As an unsaturated hydrocarbon, propene oxide constitutes one of the most important basic chemicals of the chemical industry. More than 60 % of this substance is used in the plastics sector, particularly for the production of polyether polyols for the synthesis of polyurethanes. In addition, propene oxide derivatives have an even larger 20 share of the market in the field of glycols, particularly for lubricants and antifreeze compositions.

World-wide, about 50 % of propene oxide is currently synthesised by the "chlorohydrin method". The other 50 % is obtained by "oxirane methods", and this 25 trend is increasing.

In the chlorohydrin method (F. Andreas et al.; Propylenchemie, Berlin 1969), the chlorohydrin is first formed by the reaction of propene with HOCl (water and chlorine), and propene oxide is subsequently formed from the chlorohydrin by the separation of HCl with lime. This method is costly, but when it is optimised appropriately it provides a high selectivity (>90 %) at high conversions. Chlorine losses in the chlorohydrin method, in the form of valueless calcium chloride or

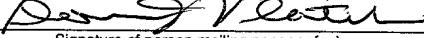
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Date of Deposit July 27, 2000

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Donna J. Veatch

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sodium chloride solutions, have hitherto led to a search for oxidation systems which are free from chlorine.

- Instead of the inorganic oxidising agent HOCl, organic compounds have been selected  
5 for the transfer of oxygen to propene (oxirane method). This indirect epoxidation is based on the fact that organic peroxides such as hydroperoxides or peroxy carboxylic acids in the liquid phase are capable of selectively transferring their peroxide oxygen to olefines with the formation of epoxides. In the course of this process, hydroperoxides are converted into alcohols and peroxy carboxylic acids are converted  
10 into acids. Hydroperoxides and peroxy carboxylic acids are produced from the corresponding hydrocarbon or aldehyde, respectively, by autoxidation with air or molecular oxygen. One serious disadvantage of indirect oxidation is the economic dependence of the value of propene oxide on the market value of the coupled product.
- 15 Using titanium silicate (TS 1) as a catalyst (Notari et al., US 44 10 501 (1983) and US 47 01 428) it proved possible for the first time to epoxidise propene with hydrogen peroxide in the liquid phase under very mild reaction conditions with selectivities > 90 % (Clerici et al., EP-A 230 949).
- 20 The oxidation of propene by a gas mixture consisting of molecular oxygen and molecular hydrogen proceeds with a low yield in the liquid phase over titanium silicates containing platinum metal (JP-A 92/352771).
- The direct gas phase oxidation of propene to form propene oxide with a selectivity of  
25 100 % was described for the first time in EP-A 0 709 360 A1 (Haruta et al.). This is a catalytic gas phase oxidation with molecular oxygen in the presence of the reducing agent hydrogen. A special titanium dioxide comprising an anatase modification which is coated with nanometre-scale gold particles is used as the catalyst. The maximum propene conversion and yield are quoted as 1 %. The Au/TiO<sub>2</sub> catalysts described  
30 achieve a propene conversion of about 1 % for a very short time only. Typical half-lives at moderate temperatures (40-50°C) are only 100-200 minutes, for example.

The regeneration of catalysts which are coated with gold and which are based on titanium silicate by dilute hydrogen peroxide solution was known hitherto (Thiele et al., J. Mol. Cat. 117, pages 351-356, 1997).

- 5 The possibility of efficiently regenerating the catalyst is of decisive importance for the development of a propene oxidation process which is of economic interest.

It has surprisingly been found that when catalysts which have become inactive are treated with water, dilute acids or dilute hydrogen peroxide solution, catalytic 10 activities of up to 80 % of the original activity can be achieved again. The catalysts which have become inactive are preferably washed with dilute acids (e.g. dilute H<sub>2</sub>SO<sub>4</sub> or HF) at a pH of 4 to 7.5, preferably 5.5 to 6.

15 The present invention therefore relates to a method of regenerating support catalysts, which are coated with gold particles and which are based on titanium dioxide or hydrous titanium dioxide, for the oxidation of unsaturated hydrocarbons in the gas phase, wherein the catalytic activity of the catalyst is regenerated by bringing it into contact with water or with dilute acid or with a dilute hydrogen peroxide solution.

20 Treatment in the sense of the present invention can be effected at room temperature or at elevated temperature. In variants of the invention, elevated pressures and/or the use of steam can advantageously be put into effect.

25 Treatment can be effected separately after removing the catalyst from the reactor, or can also be effected in the reactor if the catalytic oxidation of propene in the presence of hydrogen and regeneration of the catalyst with water or hydrogen are caused to proceed cyclically in succession. In one embodiment of this variant, it is advantageous to perform the operations of catalysis and regeneration simultaneously in a plurality of spatially separated reactors which are connected in series. These phases can be 30 connected so that they operate alternately.

Agitation of the regeneration mixture may be advantageous, but is not a requirement of the use according to the invention.

According to the invention, support catalysts can be regenerated which are coated with nanometre-scale gold particles and which are based on titanium dioxide or hydrous titanium oxide. These catalysts are preferably produced by the "deposition-precipitation" method.

The concentration of dilute hydrogen peroxide solution is usually within the range from 1 to 10 % by weight, preferably 1 to 4 % by weight.

When catalysts which are regenerated according to the invention are used for the oxidation of unsaturated hydrocarbons, there is no restriction on the amount of catalyst which is used and on the amounts of gases which are used. The "space velocity" of the gas stream through the catalyst bed should usually amount to about 0.5 to 20 l/g catalyst per hour.

The use according to the invention of regenerated catalysts is effected in the presence of the gases oxygen and hydrogen. In the presence of these gases at 150°C, the oxygenated products propene oxide and acetone are also formed in addition to the main products comprising water, propane and CO<sub>2</sub>. If the reaction temperature is reduced to <100°C, preferably to 30-60°C, the formation of water is suppressed considerably, and the formation of CO<sub>2</sub> is suppressed completely. At a temperature between 30 and 60°C only traces of the other components (about 1 % with respect to propene oxide) are found in addition to the main product propene oxide (yield about 4-5 %). The proportion of water is twice the proportion of propene oxide (molar basis).

The composition of the gas phase, which contains propene, oxygen, hydrogen and possibly an inert gas, is not only important as regards the space-time yield, but is also important as regards safety. In theory, all molar compositions of the gases propene / oxygen / hydrogen / nitrogen / inert gas (e.g. nitrogen) can be used. The preferred gas ratios for the oxidation of propene are the following ratios: H<sub>2</sub> / hydrocarbon / oxygen / nitrogen: 20-80 % / 10-50 % / 1-10 % / 0-50 %; the preferred H<sub>2</sub> / hydrocarbon / oxygen / nitrogen ratio is 30-75 % / 15-40 % / 3-8 % / 0-10 %. The molecular oxygen

which is used for the reaction can originate from diverse sources, e.g. pure oxygen, air or other oxygen/inert gas mixtures.

**Examples****Direct oxidation of propene to propene oxide**

5   **Standard reaction conditions:** the reactor was a fixed bed tubular reactor (diameter 1 cm, length 20 cm) made of double-walled glass, which was heated at a controlled temperature of 46°C by means of a water thermostat. A static mixing and temperature control section was disposed upstream of the reactor. The gold-support catalyst was placed on a glass frit beforehand. The catalyst loading was 1.8 l/g catalyst/hour. The  
10 gaseous starting materials were metered into the reactor from top to bottom by means of mass-flow controllers. The ratios of the gaseous starting materials corresponded to O<sub>2</sub> / H<sub>2</sub> / C<sub>3</sub>H<sub>6</sub> = 0.1 /1.3 /0.4 l/hour. The reaction gas mixture was analysed by gas chromatography using an FID detector (for all organic compounds containing oxygen, with the exception of CO<sub>2</sub>) and a thermal conductivity detector (for permanent gases,  
15 CO, CO<sub>2</sub> and H<sub>2</sub>O). The apparatus was controlled via a central data recording system.

The gold particle size of all the catalysts was investigated by TEM (transmission electron microscopy).

20   **Catalyst preparation 1**

100 mg H(AuCl<sub>4</sub>), dissolved in 100 ml of deionised water, were added drop-wise over 60 minutes at room temperature, with stirring, to a suspension of 10 g hydrous titanium oxide (BET specific surface 380 m<sup>2</sup>/g, sulphate content 0.6 %, 12 % water)  
25 in 0.3 l of deionised water. The pH was adjusted to 8 with an 0.5 molar Na<sub>2</sub>CO<sub>3</sub> solution in order to precipitate gold hydroxide. The slightly yellow suspension was decolorised. The suspension was stirred for 3 hours at room temperature, and the solid was separated and washed 4 times with 25 ml of deionised water each time. The solid was dried for 2 hours at 150°C and for 1 hour at 200 °C, and the dried contact catalyst  
30 was subsequently calcined in air for 2 hours at 250°C and for 5 hours at 400°C.

A catalyst which contained 0.5 % by weight gold was obtained. Characterisation by TEM showed the presence of nanometre-scale gold particles with average particle

diameters of about 1-6 nm. The results of the catalytic reaction in accordance with the standard reaction conditions (Example A) are given in Table 1.

**Catalyst preparation 2:**

5

A solution of 0.104 g HAuCl<sub>4</sub> x H<sub>2</sub>O in 400 ml distilled water was heated to 70°C and adjusted to pH 7.5 with an aqueous 0.1 N NaOH solution. 5 g titanium dioxide (an anatase-rutile mixed oxide; P 25 supplied by Degussa) was added in one portion with intensive stirring, and the batch was stirred for a further 1 hour. The solid was washed 10 5 times with 3 litres of distilled water each time, dried under vacuum at room temperature for 12 hours, and calcined for 4 hours at 400°C . A gold-titanium dioxide catalyst was obtained which contained 1 % by weight gold.

15 The results of the catalytic reaction in accordance with the standard reaction conditions (Example B) are given in Table 1.

20

**Examples 1 to 10      Catalyst regeneration and catalytic activity of gold support catalysts which had become inactive and which were treated according to the invention with water, dilute acids or dilute hydrogen peroxide solutions:**

**Example 1**

25 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H<sub>2</sub>O, stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

30 The results of the catalytic reaction are given in Table 1.

**Example 2**

5 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H<sub>2</sub>O, stirred for 1 hour at 80°C, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

**Example 3**

10 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H<sub>2</sub>O, stirred for 3 hours at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for 15 the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

**Example 4**

20 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml of 3 % H<sub>2</sub>O<sub>2</sub> solution, stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained 25 was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

**Example 5**

A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was 5 suspended in 100 ml of 6 % H<sub>2</sub>O<sub>2</sub> solution, stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

10

**Example 6**

A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was 15 suspended in 100 ml of 3 % H<sub>2</sub>O<sub>2</sub> solution, stirred for 1 hour at 50°C, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

20

**Example 7**

A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was 25 suspended in 100 ml H<sub>2</sub>O which had been adjusted with 0.05 molar H<sub>2</sub>SO<sub>4</sub> to pH 6, was stirred for 3 hours at room temperature, separated, dried for 1 hour at 150°C and calcined for 2 hours at 400°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

**Example 8**

A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was 5 suspended in 100 ml H<sub>2</sub>O which had been adjusted with 0.05 molar H<sub>2</sub>SO<sub>4</sub> to pH 6.5, was stirred for 3 hours at room temperature, separated, dried for 1 hour at 150°C and calcined for 2 hours at 400°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

**10 Example 9**

A catalyst which had become inactive due to reaction (2 g; 0.2 % propene oxide yield), and which had been produced according to *catalyst preparation 2*, was suspended in 500 ml water, stirred for 1 hour at room temperature, separated, and 15 dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

**20 Example 10**

A catalyst which had become inactive due to reaction (2 g; 0.2 % propene oxide yield), and which had been produced according to *catalyst preparation 2*, was suspended in 100 ml of 3 % H<sub>2</sub>O<sub>2</sub> solution, stirred for 1 hour at room temperature, 25 separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

**Table 1**

<b>Catalyst preparation 1</b>	<b>Time (min)</b>	<b>Propene oxide yield (%)</b>	<b>Propene oxide selectivity (%)</b>
Example A (active)	30	5.3	>97
Example A (inactive)		0.6	>97
Example 1	30	3.7	>97
Example 2	30	3.8	>97
Example 3	30	3.8	>97
Example 4	30	3.9	>97
Example 5	30	3.6	>97
Example 6	30	3.8	>97
Example 7	30	4.2	>97
Example 8	30	4.0	>97

<b>Catalyst preparation 2</b>	<b>Time (min)</b>	<b>Propene oxide yield (%)</b>	<b>Propene oxide selectivity (%)</b>
Example B (active)	30	1.4	>97
Example B (inactive)		0.2	>97
Example 9	30	0.9	>97
Example 10	30	1.0	>97

## Claims

- 5        1. A method of regenerating a support catalyst, which is coated with gold particles and which is based on titanium dioxide or hydrous titanium dioxide, for the oxidation of unsaturated hydrocarbons in the gas phase, characterised in that the catalytic activity of the catalyst is regenerated by bringing it into contact with water or with dilute acid or with a dilute hydrogen peroxide solution.

10      2. A method according to claim 1, characterised in that a catalyst which is produced by the "deposition-precipitation" method is regenerated.

15      3. A method according to either one of claims 1 or 2, characterised in that the catalyst is optionally regenerated with steam under pressure.

20      4. A method according to either one of claims 1 or 2, characterised in that an aqueous hydrogen peroxide solution of concentration up to 10 % is used.

25      5. The use of a support catalyst which is regenerated according to any one of claims 1 to 4 for the epoxidation of unsaturated hydrocarbons in the gas phase.

**METHOD FOR REGENERATING SUPPORTS CATALYSTS  
COVERED WITH GOLD PARTICLS AND USE FOR  
OXIDIZING UNSATURATED HYDROCARBONS**

**ABSTRACT OF THE DISCLOSURE**

The activity of catalysts composed of gold particles on a titanium dioxide or hydrous titanium dioxide support is regenerated by contacting those catalysts with water, dilute acid or dilute hydrogen peroxide solution. These regenerated catalysts may be used for the oxidation of unsaturated hydrocarbons.

**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

**METHOD FOR REGENERATING SUPPORTED CATALYSTS COVERED WITH  
GOLD PARTICLES AND USED FOR OXIDISING UNSATURATED HYDROCARBONS**

the specification of which is attached hereto,

or was filed on **January 7, 1999**

as a PCT Application Serial No. **PCT/EP99/00035**



I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

**198 04 711.8**  
(Number)

**Germany**  
(Country)

**February 6, 1998**  
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

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(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

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(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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